Office of FreedomCAR & Vehicle Technologies

(DOE Award Number: DE-FC26-07NT43277)

PROJECT CLOSE-OUT TECHNICAL REPORT

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PROJECT TITLE: Multi-Component Nanoparticle Based lubricant Additive to Improve Efficiency and Durability in Engines

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Acknowledgment

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Project Objective:

High-level objective of this project is to develop nanoparticle based additive technology to improve friction and wear characteristics of engine oil with a long-term focus to enhance durability and efficiency of engines. The project encompasses a detailed investigation of various chemicals that favors stable boundary film formation and therefore reduce friction and wear of engine components. These active chemicals designed as nanomaterials will be surface-stabilized to gain maximum dispersion stability in a lubricant media. This effort shall be focused with the following objectives in mind: develop active nanoparticle composite, optimize process design, detailed tribological testing and surface characterization, physical and chemical characterization of nanomaterials, and limited component level testing to document friction and wear improvements. Additional motivation is to minimize sulfur / phosphorous contents and lower ash forming components in additives and therefore improve aftertreatment functioning and emission.

This effort shall be focused, over a two year funding period: Phase-I will be primarily a feasibility study, which includes selection of components for active nanoparticles, design and formulation, and synthesis of the active nanoparticles, optimize process design, physical and chemical characterization of nanomaterials, tribological testing and document friction and wear improvements. As a continuous effort of the Phase-I, Phase-II will focus on the optimization of the identified nanoparticle-based additives specifically for DOE strategic goal - minimizing S and P contents in additives and lowering ash-forming components. Additional efforts will also be invested in

extended component level tribo-testing, manufacturing process scale-up, cost evaluation, and commercial viability assessment.

In boundary lubrication, mating surfaces in direct physical contact are in surface asperities dimensional scale. These conditions may benefit from the nanometric size of the advanced nanoparticle lubricants in the following ways: (1) by supplying nano to sub-micron size lubricating agents which reduce friction and wear at the asperity contact zone, (2) by enabling strong metal adsorption and easy wetting, (3) by reacting with the surface to form durable lubricating "transient transfer" films, sustain high loads and also retain under high temperatures, and (4) by enabling all these at minimal cost and great environmental safety. Suitably designed nanomaterials can significantly lower sulfur and phosphorus level in the lubricant additive pack, and therefore positively impact after-treatment catalyst life and exhaust emissions.

Project Scope:

The project will develop application specific active nanostructures of inorganic dry solid lubricant intercalated with active organic molecules for engine oil. These materials shall consist of layered pressure sensitive inorganic nanoparticles of molybdenum disulfide (MoS_2) that is functionally attached to suitable organic temperature sensitive molecules that are effective in boundary lubrication to reduce friction and/or wear. The resulting nanomaterial additive will be designed for low ash, sulfur, and phosphorus content, preferably using an environmentally acceptable synthesis process.

The effort shall include development and optimization of a chemo-mechanical process to generate multi-component nanoparticle additive that is suitably stabilized and

dispersed in oil. Physical and chemical characterization of these materials shall be done using a range of microscopic and surface analytic tools. Focus shall be on understanding surface passivation and dispersion mechanism in hydrocarbon media for extended lubricant shelf-life. Extensive laboratory-based tribological evaluation of nanomaterials will be performed to document friction and wear characteristics in boundary lubrication regime. Following bench test results, the additive will be evaluated using single cylinder engine test to document efficiency and durability. Extensive market survey and industrial/economic impacts of nanoparticle based additive technology will be conducted.

The project activities as outlined in the SOW for the funding phase October 1, 2007 – September 30, 2008 are listed below. [*To be noted: most of these activities are overlapping in nature on the time-scale and are being led by Co-PIs with support from other team members*].

1. Selection and design of multi-component nanoparticle based additive for engine applications. (*Timeline: Oct'07 – Mar'08*)
2. Synthesis of the nanoparticle-based additives (*Timeline: Nov'07 – Jul'08*)
3. Detailed characterization of synthesized nanoparticles for shape, size and chemistry and optimize these parameters (*Timeline: Jan'08 – Jul'08*)
4. Design and execution of application-specific bench scale tribological tests to simulate engine conditions (*Timeline: Apr'08 – Sep'08*)

Major Activities: Phase 1 (October 1, 2007 – September 30, 2008)

Task 1: Selection criteria for improving lubrication formulation to enhance engine efficiency

Selection of the active materials for nanoparticle design is critical for their ability to form stable boundary films under a suitable parametric window of temperature and pressure. Friction reduction in critical engine components will improve engine efficiency while low wear will lead to component durability. Selection of amphiphilic molecules will promote high metal surface adsorption, and have demonstrated low wear and friction characteristics. In addition, inclusion of S and P based chemistry facilitates the formation of stable tribofilms. However, presence of active S and P in exhaust stream has negative effect on the aftertreatment catalyst and devices (DPF). To balance the requirement for wear and friction reduction, and for minimizing the -ve effects of P and S, a formulation with reduced amount of P and S would be a desired option.

Key Results and Findings:

Based on the team's current understanding and experience on compounds that positively impact friction and wear characteristics (namely P and S based chemicals), materials were selected for the designing stage. Molybdenum disulfide (MoS_2) is the core nanoparticle and other P-based compounds are used as nanoparticle stabilizers. Selection of an 'amphiphilic' molecules was useful as it helped to form thin film and demonstrate very low wear and friction characteristics. Other critical performance characteristics of the additive taken into consideration during discussion and selection of the active materials are: antioxidation characteristics, hydrolytic stability, low ash forming composition, preferably environmentally sustainable etc. The main driver for this

component selection was to develop a low SAPS (sulphated ash, phosphorus and sulfur) nanoparticle based additive technology.

A wide category of nanoparticles has been explored for its potential roles as AW additives to reduce wear and/or friction. These materials include (1) pure metals such as Cu, Ag, Al-Sn, and Mo, are characteristics of malleability under shear loads; (2) certain oxides like SiO_2, ZrO_2, SnO_2, SiO_2-MgO, ZnO; (3) LaF_3, C_aCO_3, CeF_3, PbS, MoS_2, WS_2, and (4) other including nanostructured or nanosized diamond particles, inorganic borates (sodium & potassium borates) and PTFE. Elements Si and K tend to diffuse and form glassy phases with low melting point; Zn will react with catalyst washcoat at about 600 ^oC. In a separate approach, the team has identified inorganic nanoparticle with possible addition of metallic dopant and/or intercalated with organic molecules. After learning high temperature and oxidation requirements of the intended application, the following candidates were considered for the above design: Inorganic core: MoS_2; Metallic dopant: Silver (Ag); Organic active agent containing P and B group. Environmental and potential non-toxicity issues also influenced the selection of these elements.

Task 2: Synthesis and designing of active nano particulate lubricant

MoS_2 is one of the promising materials due to its strong affinity for metal surfaces and film forming characteristics. In a suitable compounded form with phosphorus, they can undergo chemical transformation at the metal surface (Fe) to form Fe-phosphate based glassy film that absorbs most of the shearing load of contacting surfaces. In addition to its general (1) anti-wear efficiency (2) good film strength (3) relatively high temperature resistance, and (4) self-lubricating properties, Mo-based compounds have found tremendous use in additive formulations because of its low cost to benefit ratio.

Using a top-down mechanical shearing synthesis process, MoS_2 particles can be micronized to nano-dimensions and suitably dispersed with the help of an amphiphilic molecule in a hydrocarbon media for extended shelf life. Additionally, inclusion of elements such as Ag, B, P etc. are expected to improve nanoparticle lubrication characteristics.

Experiment was designed to develop the desired nanomaterials using the chemo-mechanical process. In Phase-I, the focus has been mainly on exploring the effects of process conditions (*process medium, environment condition, process time*) on particle size and agglomeration. Further, using few procedural changes using the same material combination, effort was made to develop a cost effective production process by either reducing the required time of sample processing or improving the quantity of output. Nanomaterials were fully characterization to develop correlation between the processing time and particle size. The experimental results have validated that the proposed process, at least at lab scale, is repeatable. The produced MoS_2 particles have an average size of about 200 nm (*on number basis*).

The design includes preparation of inorganic nanoparticle of MoS_2 with possible addition of metallic dopant (silver nanoparticles) and/or intercalated with boron-based organic molecules (boron amide or potassium triborate).

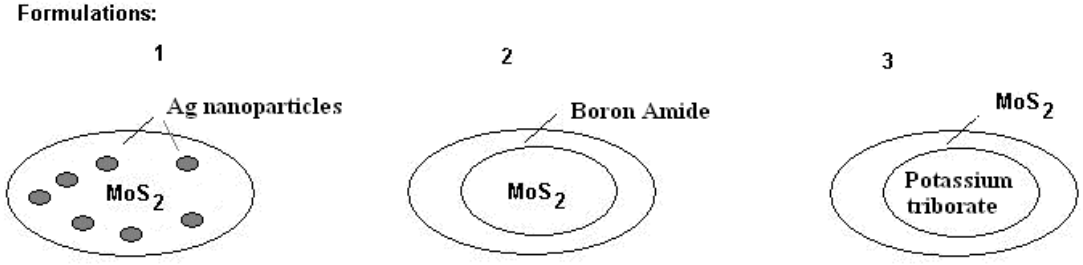
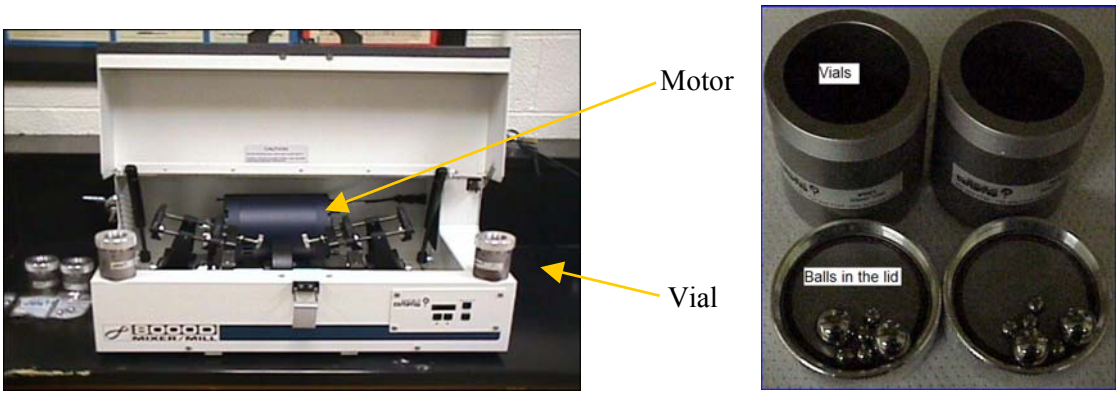


Fig.1: Designed Formulations

Key Results and Findings:

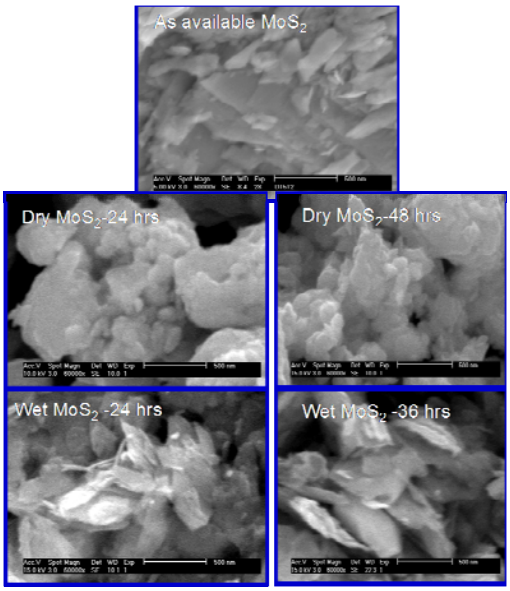
The current approach of nanoparticle synthesis involved a top-down chemo-mechanical process to break down MoS_2 particles (*commercially available in the particle size range of 4-5 μm*) to mean particle size range of 200 nm. The lamellar structure of MoS_2 provided effective lubrication in a wide range of loads, in many cases exceeded 250,000 psi. The lubrication mechanism was through the formation of layered MoS_2 planes that have low shear inter-planner bonding energy. In an earlier study, synthesized MoS_2 nanoparticles were dispersed in a few organic media and have shown lubrication potentials as long as the particles were integrated with organic molecules and effectively dispersed. MoS_2 was the primary choice of inorganic material. An amphiphilic molecule was the organic medium for integration. Metallic components (mainly Ag) and boron-based compounds were introduced as composite nanoparticle systems for tribo-testing.

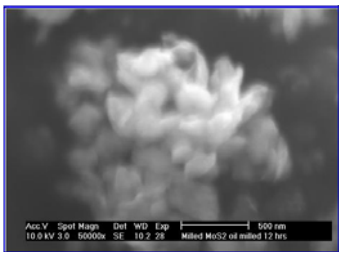
In a mechanical milling process, the target material (commercial MoS_2) was broken down to smaller particle size through mechanical impaction process.



Mechanical millings led to lamellar layered structure of MoS2 when thermal diffusion caused the adjacent layers to physically and chemically bind and resulted in alloying. In a separate study, milling in different media (air, alcohol and a hydrocarbon

based fluid) resulted in particles with different shape and structures that were analyzed using SEM image analyzer. It was observed due to increase in surface energy during particle size reduction, clusters were formed. There was however a critical particle size beyond which any further size reduction resulted in increased particle clustering. Milling process in air generally led to smaller and rounded particle size, whereas organic media retained the original particle structure. A combination of dry and wet ball milling was selected to generate particles with coated hydrocarbon layer and prevent the clustering process. The following series of SEM images and figures illustrates these phenomena.





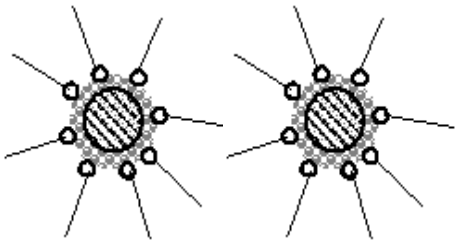
Particle clustering due to high surface energy

MoS_2 ball milled in air for 24 and 48 h showing particle size reduction and clustering

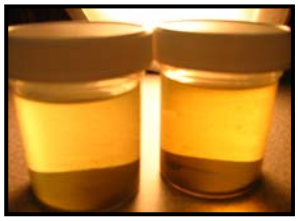
MoS_2 ball milled in alcohol / oil for 24 and 48 h showing particle structure retention

Composite nanoparticles produced through hybrid process in presence of an ampliphilic molecule (canola oil) resulted in adequate particle surface stabilization. The process significantly reduced particle surface energy and clustering to extend lubricant shelf life. It was unclear at this point if intercalation of adjacent layers MoS_2 with hydrocarbon molecules occurred under the current experimental conditions. Further study was required to determine if particle energetic and chemical interaction played a role in intercalation process.

An extension of the hybrid process involved breaking down the particles in air media and followed by milling in presence of a select chemical agent. The advantages are - it not only reduced the particle size, but also retained the crystalline character of the MoS_2 particles. This largely prevented crystal structure breakdown (amorphization) and lattice defects that are prone to occur in high-energy mechanical shearing process if run for significantly extended time without strictly controlling the gas environment.



Stability is enhanced by increased electrostatic repulsion between particles and physical separation by



Unstabilised nanoparticle

Stabilized nanoparticle

Development of active multi-component nanolubricant materials:

The team has identified a multi-component nanoengineered inorganic and organic hybrid system with possible addition of metallic dopant and suitable organic agent:

Inorganic CoreMetallic	**dopant**	**Organic active agent containing phosphorus and boron group**
MoS_2	Silver (Ag)	Boron Ester or Amide

The synthesis procedures were based on the hybrid milling process (dry milling step was followed by wet (oil) milling step) to integrate active multi components (e.g., B, Ag) using the chemo-mechanical process for formulations of specific interest (See Fig.1).

1) Hybrid milled MoS_2 with silver nanoparticles in oil
2) Hybrid milled MoS_2 with boron amide in oil
3) Hybrid milled MoS_2 with potassium triborate in oil

The nanoparticle additives were prepared by two routes, i.e., the proposed 48h dry processing followed by 48h wet processing for nanoparticle-I, 12h dry processing followed by 30 minutes of ultrasonication for nanoparticle-II.

Significant Conclusions and Accomplishments:

1. Mechanical ball milling process can produce nanoparticles using a 'top-down' approach
2. Milling process in different media has significant impact on the structure and size of the particles. Milling in air reduces the particle size of MoS_2 whereas milling in organic media retains the original structure of MoS_2
3. MoS_2 particle undergoes mechanical alloying of adjacent layers through thermal diffusion process
4. Surface energy and particle agglomeration is largely reduced when milling is done in polar hydrocarbon media.
5. Stabilized nanoparticles can significantly improve friction and wear behavior.
6. The samples of proposed formulations are nanoparticles of multicomponent system which include:
    a. Molybdenum sulfide (good solid lubricant at moderate temp. <350°C)
    b. Silver nanoparticles (form silver molybdate, is a good lubricant at high temperature >400°C)
    c. Boron-based additive (potassium borate and boron amide are good extreme pressure additives)
7. Application of proposed formulations is developed to reduce or eliminate the current level of phosphorous-based additives in oil

8. Three multi-component system additives (Ag doped MoS_2, hybrid milled MoS_2/boron amide, and hybrid milled MoS_2/potassium triborate) were prepared and tested in laboratory conditions.

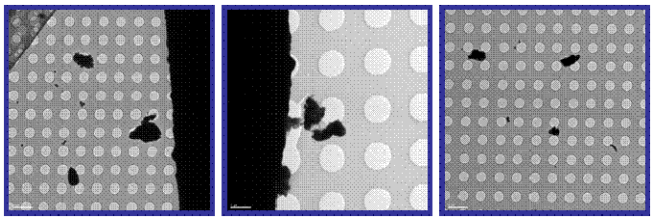
Task 3: Detailed characterizations of synthesized nanoparticles for shape, size and chemistry and optimize these parameters

The team has used a variety of analytical tools to monitor particle size, shape and morphology during the processing and development stage. It was observed that a detailed understanding of the particle morphology was critical for design and optimization. Besides already used techniques for analysis of nanoparticles (TEM, XRD, SEM), few new techniques were developed and applied during this period. Particle size analyzer from Horiba provided particle size distribution and XPS provided chemical structure of the film formed during tribo-testing. Infrared (FTIR) and Raman Spectroscopy are useful tools to study chemical bonds of lubricant (*Mo-S and S-S bond as an indicator of the MoS_2 presence*) or study interaction between lubricants and base oils.

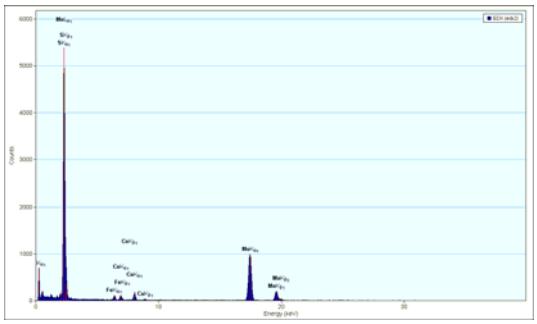
Key Results and Findings:

Effect of mechanical processing time on particle size reduction:

Average particle size of commercial as-received MoS_2 particles determined using particle size analyzer was in the range of 2~5 μm. This was further corroborated using transmission electron microscope (TEM, Titan 80-300S). The elemental composition of as-received MoS_2 was also quantified by EDX on the TEM. Clearly, the as-received MoS_2 powder did not contain any O; the other elements present in the spectrum came from the copper mesh, which was used for sample preparation.



TEM images showing the particle and clusters of as-received MoS_2 powder (Scale bar: 2 µm)



Spectral showing EDX analysis results of the element composition of as-received MoS_2 powder

Effect of mechanical shearing time on MoS_2 particle size was determined using particle size analyzer. It was observed that the size reduction was significant (2.24 µm to 0.69 µm) during the first 12 hrs, and the effectiveness decreased beyond that period (0.69 to 0.60 µm). Overall, the mechanical shearing process was very effective in reducing the particle size of MoS_2.

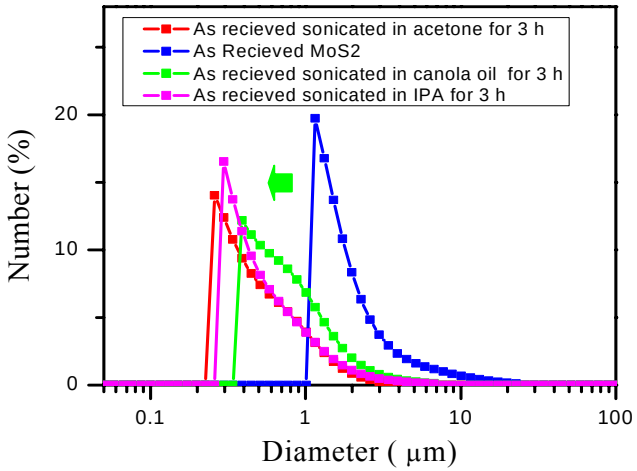
PROCESS	AREA cm^2/cm^3	MEAN (µm)	MEDIUM (µm)	Diameter (µm)		
				10%	50%	90%
As Received (AR)	3531	2.23978	1.50646	1.076	1.5065	4.0217
AR + mechanical shearing (12h)	23841	0.6916	0.525	0.2917	0.5250	1.2694
AR + mechanical shearing (48h)	23847	0.60259	0 .48327	0.2929	0.4833	1.0446

Effect of mechanical processing time on MoS_2 particle size reduction

Effect of ultrsonication process on as-received MoS_2 powders in different types of fluids:

Sonication is a widely used technique to de-agglomerate or break down clusters of primary particles. Experiments were designed to study the effect of dispersants on the de-agglomeration phenomena. Surface stabilized and de-agglomerated nanoparticles will

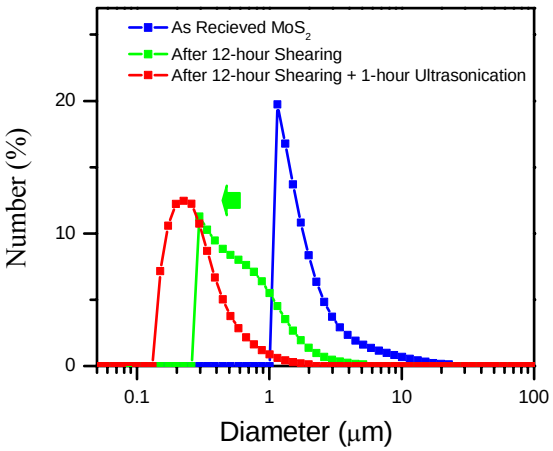
impact the shelf life of the final product. It was indicated that dispersants have moderate effect on de-agglomeration. Figure below presents the particle size analysis of the sonicated samples.



Particle size distribution curve for MoS_2 particles in as-received form, and sonicated in acetone, IPA, and fatty acid, respectively.

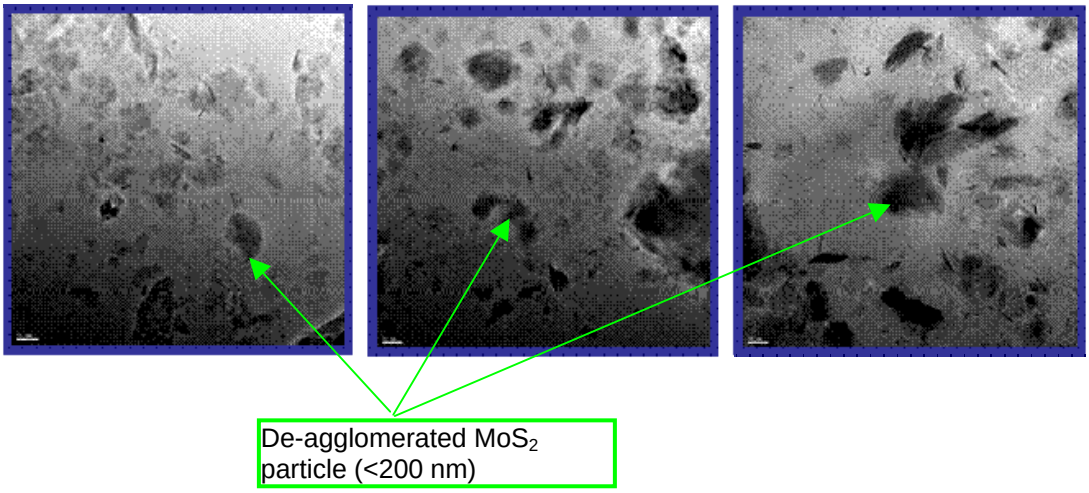
Combined effect of mechanical shearing and ultrasonication on MoS_2 particle size reduction and de-agglomeration:

An optimized combination of the particle size reduction and de-agglomerization using sonication could potentially lead to size reduction and dispersion. Particle size distribution for the processed MoS_2 particles showed 12-hour shearing has effectively reduced the particle size. De-agglomerated particles showed an APS of about 300 nm.

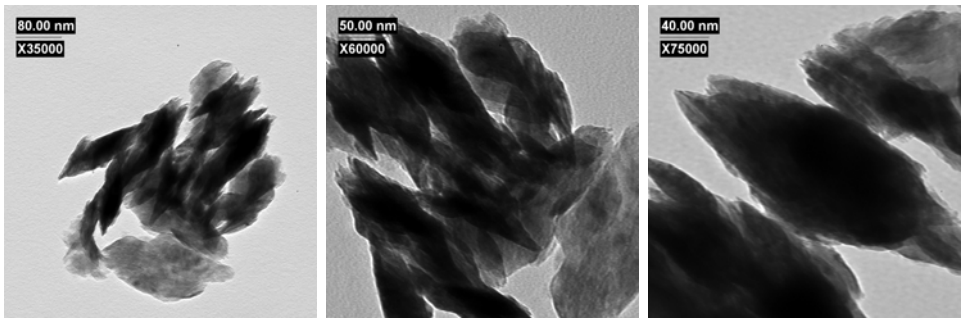


Particle size distribution curve for MoS_2 particle in as-received form, after 12-hour shearing, and after 12-hour shearing followed by 1-hour ultrasonication

TEM analysis confirmed the particle size analysis results. Figure below shows the TEM images with typical particle size or cluster size of 200 nm.



Top-down chemo-mechanically processed MoS_2 samples (*prepared by dry milling, wet milling, or hybrid milling*) were studied using TEM. Samples prepared by optimized hybrid process (36h dry+36h wet milling) showed formation of well-uniform ellipsoidal particles with extruded ends. With longer milling time (48h dry+48h wet) particles were extruded further and in some cases were elongated significantly.



TEMs of hybrid milled MoS_2 with 36 h dry milling followed by 36 h oil milling (Low viscosity PAO-10 oil)

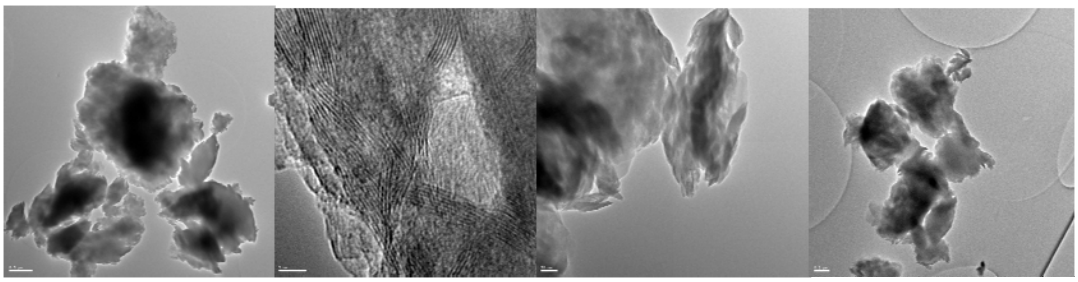
Metallic Ag nanoparticle doping:

Ag is a good lubricant itself. Silver doped of Mos2 nanoparticle was achieved using 3 different pathways:

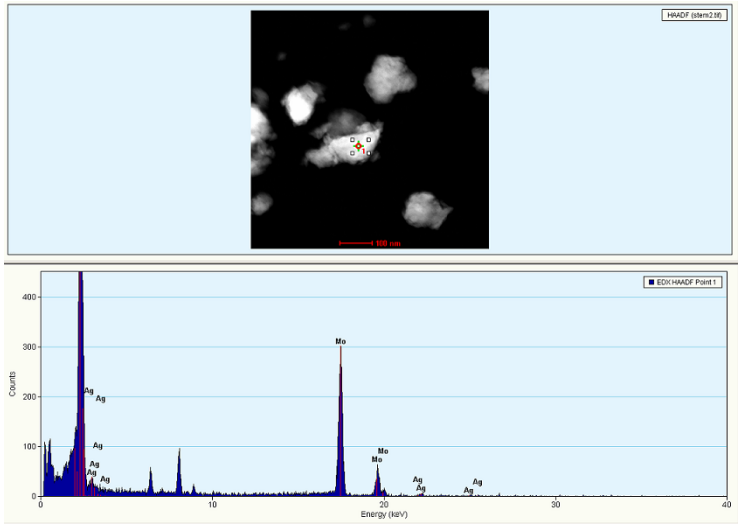
Method 1 – Separate preparation of MoS_2 nanoparticles by milling and silver metal nanoparticles by reduction, followed by combination of MoS_2 and silver nanoparticles;

Method 2 – Synthesis of MoS_2 nanoparticles by high-energy milling followed by addition of silver salt and its reduction;

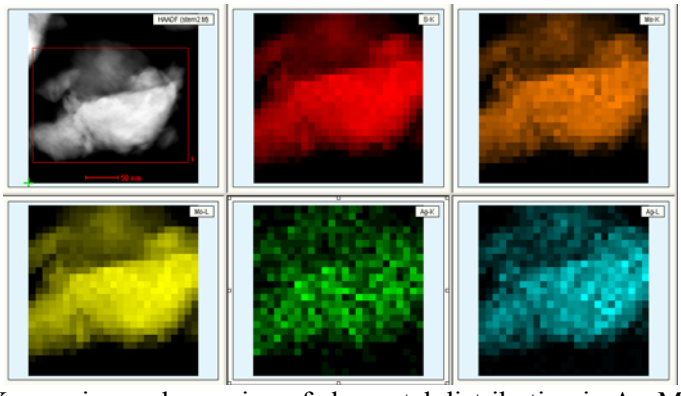
Method 3 – Combined milling of silver salt and molybdenum disulfide followed by silver salt reduction.



TEM graphs of Ag-MoS_2 nanoparticles; TEM pictures of sample prepared by Method 2 show less aggregated particles with uniformed ellipsoidal shapes and comparatively higher monodispersity.



STEM/EDX elemental analysis pattern of dry milled Ag-MoS_2 particles

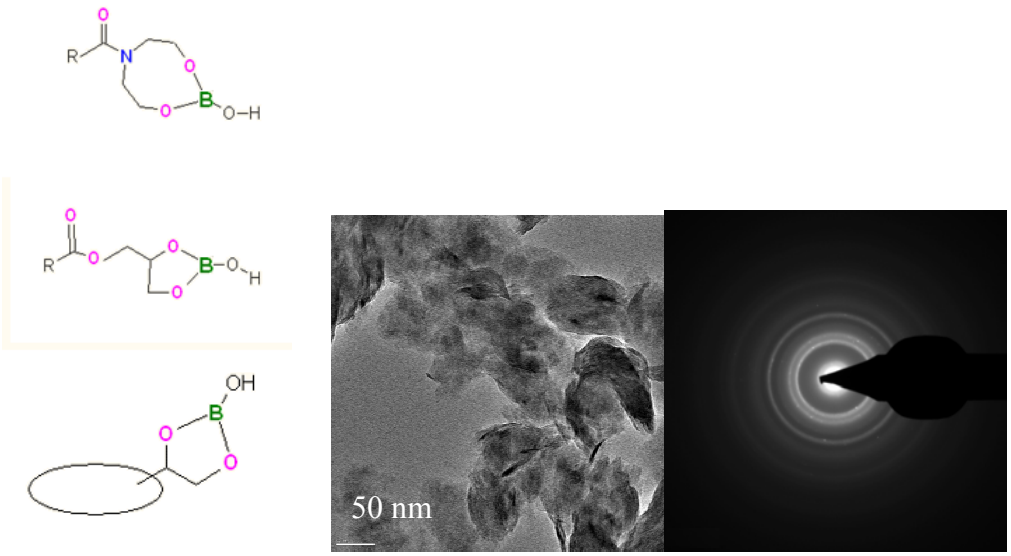


STEM/EDX scanning and mapping of elemental distribution in Ag-MoS_2 particle

EDX scanning showed a good dispersion of silver nanoparticles in MoS_2 and direct dependence between density of MoS_2 and silver density (brighter intensities in figures above).

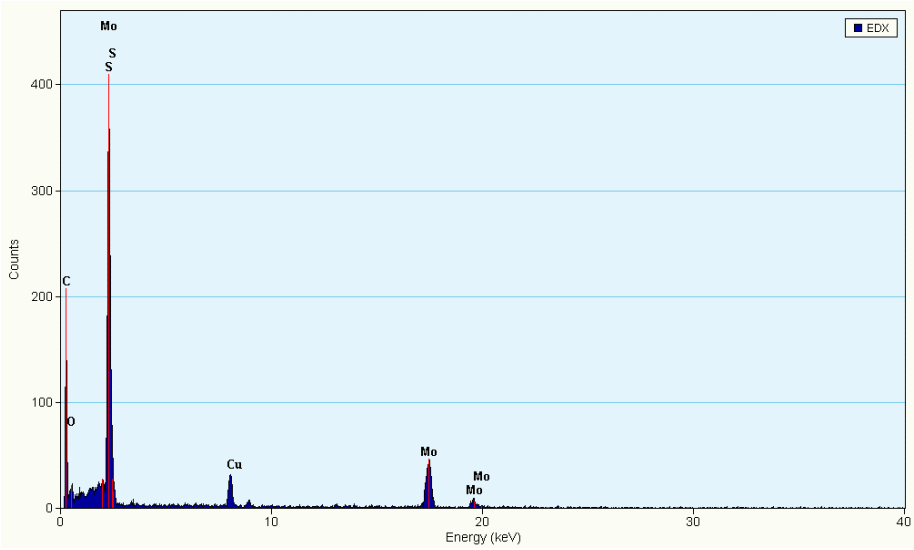
Hybrid milled MoS_2 with boron amide

Borate ester, which is based on boron alkyl diethanol amides and mono glycerides, showed good antiwar performance and in some cases exceeded the ZDDP performance. Hybrid milled MoS_2/boron amide nanoparticles were characterized using TEM, EDX, STEM, and PSA techniques. The hybrid milling procedure allowed synthesis of uniform ellipsoidal open-ended structures of MoS_2 nanoparticles. The diffraction pattern confirmed that prepared samples were polycrystalline and consisted of small crystalline particles. The TEM image (below) shows a MoS_2-Boron amide nanoparticle.



Chemical (boron alkyl diethanol amides and mono glycerides, where R – carbon chain C7-C17, borated diols coordinates with metal surface)

EDX analysis confirmed the elemental composition of MoS_2 particles with boron amide additive (*carbon and oxygen elements from boron amide groups are present on the EDX pattern, while boron and nitrogen elements are 'light elements' which cannot be detected by EDX, copper peaks correspond to copper grids*).



EDX pattern of hybrid milled MoS_2/boron amide nanoparticles

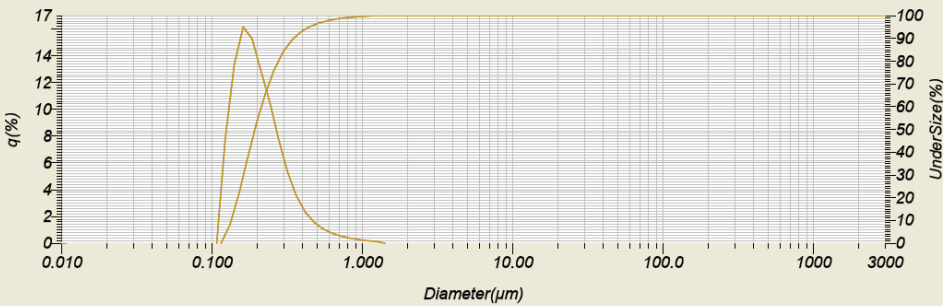
Particle size analysis using HORIBA laser scattering particle size distribution technique confirmed nanoparticles were in desired size range. The particle distribution by number and volume gives better understanding of the samples. The particles had mean size of 230 nm and 90 % of particles were smaller than 350 nm.

HORIBA Laser Scattering Particle Size Distribution Analyzer

Horiba LA950 for Windows [Wet] Ver4.11

UNIVERSITY of ARKANSAS

ID#	: 200806181114737		
Sample Name	: MoS2 107-2 Vanlube in isopropanol		
Material	:	Median Size	: 0.19215(μm)
Source	: University of Arkansas	Mean Size	: 0.22677(μm)
Lot Number	:	Mode Size	: 0.1621(μm)
Circulation Speed	: 5	Diameter on Cumulative %	: (1)10.00 (%)- 0.1338(μm)
Ultra Sonic	: 03:19 (5)		: (2)50.00 (%)- 0.1922(μm)
Agitation Speed	: 4		: (3)90.00 (%)- 0.3480(μm)
Transmittance(R)	: 85.9(%)		
Transmittance(B)	: 80.0(%)		
Refractive Index (R)	: MoS2 in isopropanol[Molybdenum sulfide(3.600 - 0.100i),2-Propanol(1		
Distribution Base	: Number		
Iteration Number	: 15		



No.	Diameter(μm)	q(%)	UnderSize(%)	No.	Diameter(μm)	q(%)	UnderSize(%)	No.	Diameter(μm)	q(%)	UnderSize(%)	No.	Diameter(μm)	q(%)	UnderSize(%)
1	0.011	0.000	0.000	28	0.445	2.311	95.162	55	17.377	0.000	100.000	82	678.504	0.000	100.000
2	0.013	0.000	0.000	29	0.510	1.549	96.711	56	19.904	0.000	100.000	83	777.141	0.000	100.000
3	0.015	0.000	0.000	30	0.584	1.063	97.774	57	22.797	0.000	100.000	84	890.116	0.000	100.000
4	0.017	0.000	0.000	31	0.669	0.745	98.519	58	26.111	0.000	100.000	85	1019.515	0.000	100.000
5	0.020	0.000	0.000	32	0.766	0.529	99.048	59	29.907	0.000	100.000	86	1167.725	0.000	100.000
6	0.022	0.000	0.000	33	0.877	0.376	99.424	60	34.255	0.000	100.000	87	1337.481	0.000	100.000
7	0.026	0.000	0.000	34	1.005	0.265	99.689	61	39.234	0.000	100.000	88	1531.914	0.000	100.000
8	0.029	0.000	0.000	35	1.151	0.184	99.874	62	44.938	0.000	100.000	89	1754.613	0.000	100.000
9	0.034	0.000	0.000	36	1.318	0.126	100.000	63	51.471	0.000	100.000	90	2009.687	0.000	100.000
10	0.039	0.000	0.000	37	1.510	0.000	100.000	64	58.953	0.000	100.000	91	2301.841	0.000	100.000
11	0.044	0.000	0.000	38	1.729	0.000	100.000	65	67.523	0.000	100.000	92	2636.467	0.000	100.000
12	0.051	0.000	0.000	39	1.981	0.000	100.000	66	77.339	0.000	100.000	93	3000.000	0.000	100.000
13	0.058	0.000	0.000	40	2.269	0.000	100.000	67	88.583	0.000	100.000				
14	0.067	0.000	0.000	41	2.599	0.000	100.000	68	101.460	0.000	100.000				
15	0.076	0.000	0.000	42	2.976	0.000	100.000	69	116.210	0.000	100.000				
16	0.087	0.000	0.000	43	3.409	0.000	100.000	70	133.103	0.000	100.000				
17	0.100	0.000	0.000	44	3.905	0.000	100.000	71	152.453	0.000	100.000				
18	0.115	0.000	0.000	45	4.472	0.000	100.000	72	174.616	0.000	100.000				
19	0.131	8.021	8.021	46	5.122	0.000	100.000	73	200.000	0.000	100.000				
20	0.150	13.403	21.424	47	5.867	0.000	100.000	74	229.075	0.000	100.000				
21	0.172	16.166	37.590	48	6.720	0.000	100.000	75	262.376	0.000	100.000				
22	0.197	15.286	52.875	49	7.697	0.000	100.000	76	300.518	0.000	100.000				
23	0.226	12.869	65.745	50	8.816	0.000	100.000	77	344.206	0.000	100.000				
24	0.259	10.544	76.289	51	10.097	0.000	100.000	78	394.244	0.000	100.000				
25	0.296	7.751	84.040	52	11.565	0.000	100.000	79	451.556	0.000	100.000				
26	0.339	5.304	89.343	53	13.246	0.000	100.000	80	517.200	0.000	100.000				
27	0.389	3.507	92.850	54	15.172	0.000	100.000	81	592.387	0.000	100.000				

Significant Conclusions and Accomplishments:

1. A top-down chemo-mechanical hybrid process was developed for designing multicomponent MoS_2 based composite nanoparticles (particle size range of 100-200 nm) for lubricant additive application

2. A unique hybrid chemomechanical process for surface stabilization was developed to effectively disperse nanomaterials in hydrocarbon media and improve shelf life
3. Critial parameter selection for process optimization was employed (milling media, time, environment etc.) to obtain consistent nanoparticles of desired particle size
4. Multiple analytical tools (SEM, STEM-EDX, XRD, AFM, particle size analyzer, FTIR etc.) were deployed to characterize particles and establish their shape, size and morphological features for effective lubrication

Task 4: Design and execution of application-specific bench scale tribological tests to simulate engine conditions

The main objective of the tribological studies was to develop an extensive database on the friction and wear performance of various oil blends that were formulated with active nanostructured MoS_2 at various additive concentrations. The substrate materials were AISI 52100 steel and cast iron (*as they are more representative of the actual liners used in engines*). Detailed tribological tests offered a basic understanding of the lubrication mechanisms involved and the role of active nanostructure MoS_2 in friction and wear.

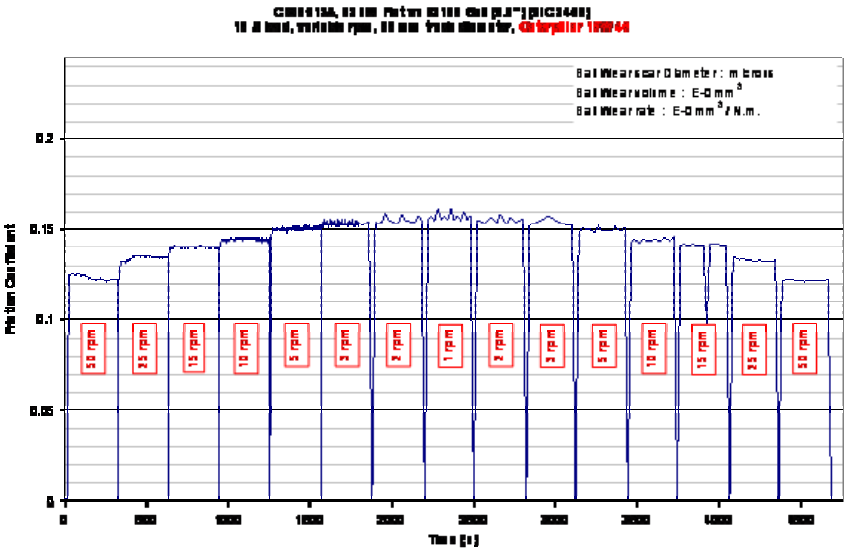
Key Results and Findings:

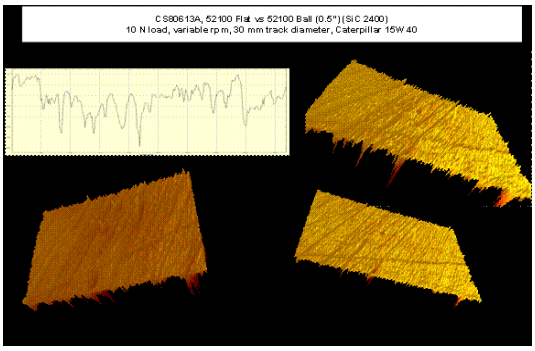
Ball on disk test rig was used to identify the required load, speed conditions to generate boundary-lubricating conditions. The different loads applied were 1, 2, 5 and 10N and the rolling speed used were 25, 15, 10, 5, 3, 2, 1 rpm. The intension was to understand frictional behavior of those systems under different max Hertzian contact pressures with variable speed and controlled (fixed) surface roughness. After scanning

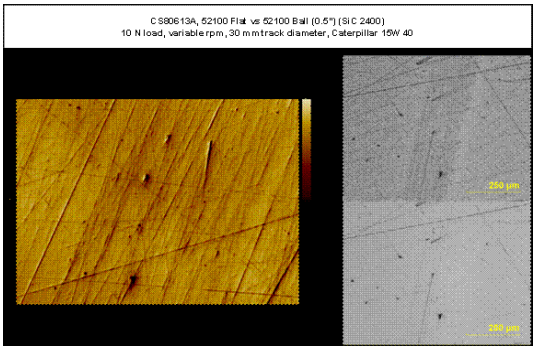
the load 10-5-2-1 with ½" diameter ball, it was decided to flatten the ball surface. Flattening the ball surface basically increases the radius of curvature of the tested ball surface. Flattened ball measured radius of curvature: 40 mm 5 N load: 190 MPa

The following data shows the summary of representative tests performed using the above test conditions:

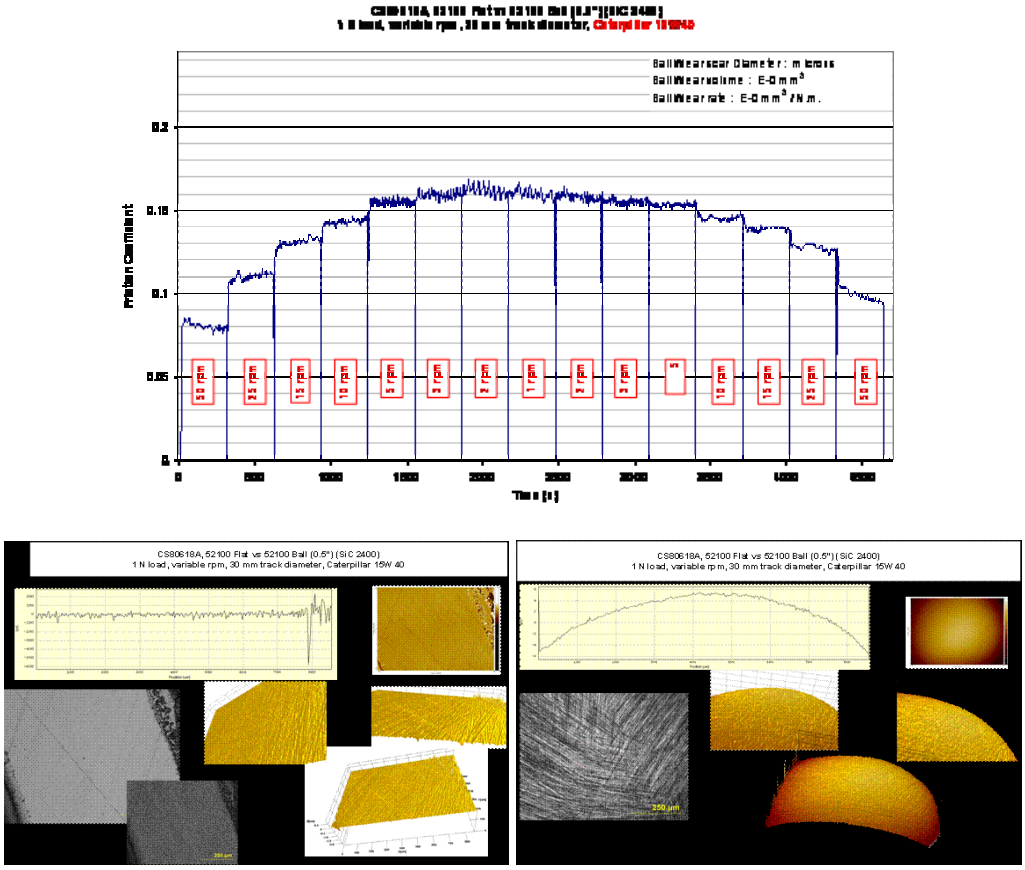
1. *Friction coefficient using 52100 flat vs. 52100 ball (1/2 inch dia) 10N load, variable rpm and 30 mm track diameter. Using 15W40 oil*







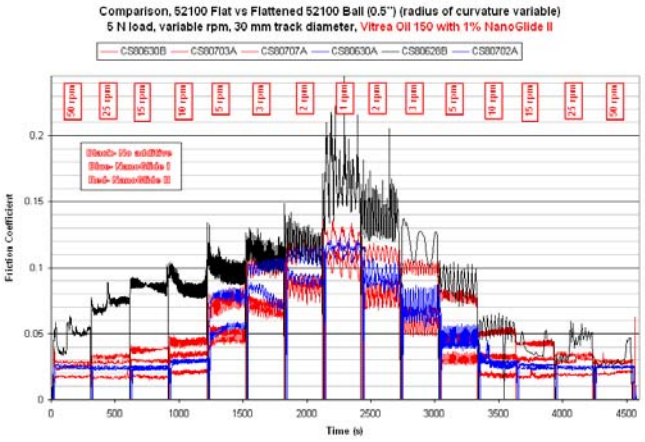
2. *Friction coefficient using 52100 flat vs. 52100 ball (1/2 inch dia) 1N load, variable rpm and 30 mm track diameter. Using 15W40 oil*



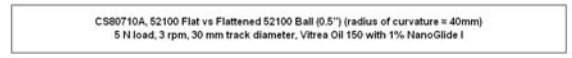
This procedure helped to select the right test conditions for boundary lubrication. In this method the speed was varied during the test under constant load. In the first case (10N load) there was minimal difference observed between the various speeds stages, that was resolved when 1N loading was used.

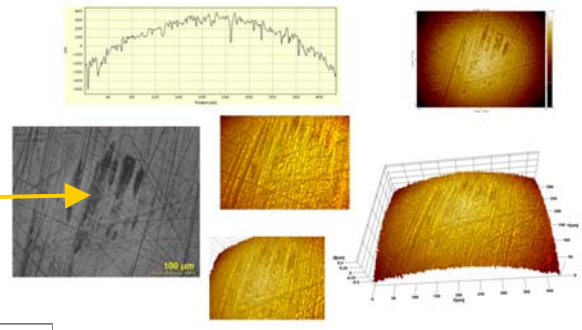
Preliminary test data indicated a 20 – 30% improvement in the friction coefficient (*using ball-on-disk test configuration*) when compared with a mineral base oil of similar viscosity as the baseline engine oil. In a separate study, 4-ball wear test data indicated a 50% improvement in wear scar using industry specified test conditions (*ASTM D 4172*). Composite Boron amide/MoS_2 nanomaterials showed significant improvement in wear.

Figures below summarize the hi-points of tribo-tests:

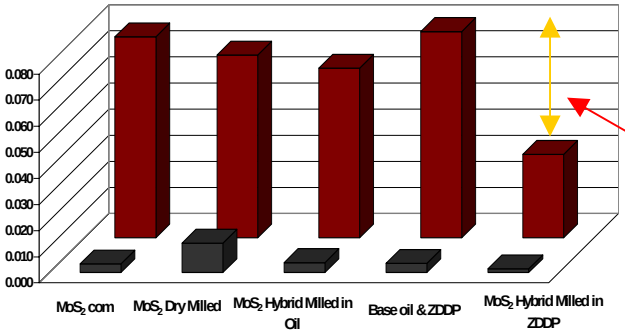


20 - 40% reduction in COF in BL regime

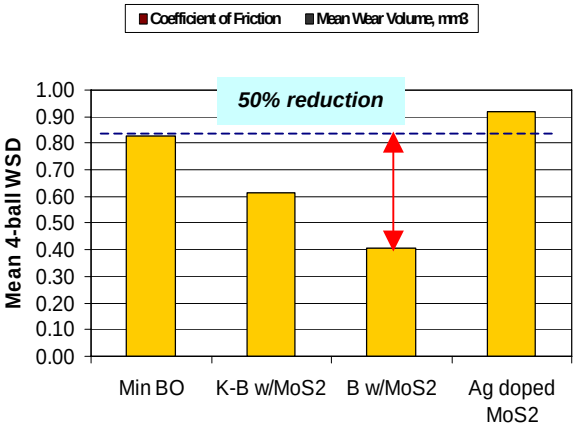




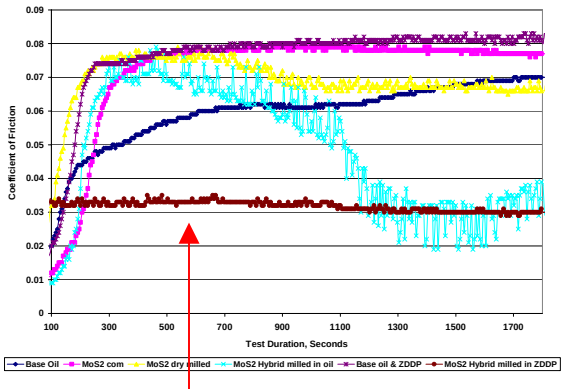
Evidence of MoS_2 transfer layer on surface



50% reduction in COF by using nanomaterials when compared without it in presence of ZDDP additive



Boron-MoS_2 nanoparticle give 50% reduction in wear

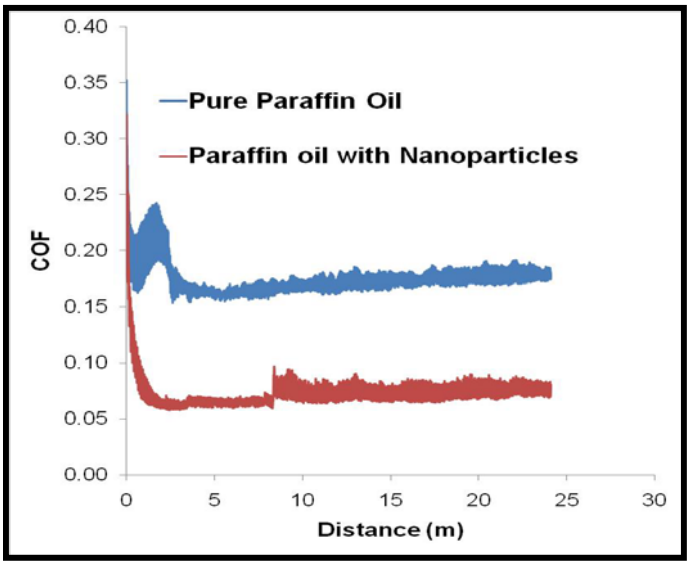


Nanomaterials are effective in reducing COF from the very first operating cycle

3. Preliminary extended duration tribological testing:

Coefficient of friction was measured for MoS_2 nanoparticles in paraffin oil. MoS_2 nanoparticle additives were prepared using dry milling and an emulsifier containing phosphorus (2 wt. %) and pure paraffin oil was used to stabilize and disperse the particles using high-powered sonication. Emulsifier was added to enhance nanoparticle dispersion in paraffin oil.

The test was conducted under low speed (*0.25 cm/s*) and high contact pressure (0.25 cm/s) to simulated boundary lubrication conditions. Long duration tests were run for 1750 laps and continued for more than 12 hours to study the durability of the nanoparticles generated transfer films and its sustainability under severe conditions. The figure below presents the resulting COF from 25m distances travelled; the values did not change even after 131 m, 1750 laps, and 12 hrs. Based on preliminary tribological results, presence of nanoparticle additives reduced the friction coefficient to 0.075, as compared to 0.175 for pure paraffin oil.



This shows the COF results for 6 mm 52100 steel ball, disc 4340 steel (machined surface), 25 m distance, 10 N load, 0.25 cm/s, 1.43 GPa.

Significant Conclusions and Accomplishments:

1. A parametric window of load and speed was identified to perform tribo-tests for designed nanomaterials under boundary lubrication regime.
2. Suitable surface analytical and measurement techniques (SEM, 3D surface profilometry, TEM, microscopy etc.) were identified to quantify improvements derived from using nanoparticles in reducing wear and friction of laboratory specimens.
3. Nanoparticles of MoS_2 in the stabilized form was able to reduce the fiction coefficient of mineral base oil by 20 – 40%
4. Measured wear scar diameter of 52100 steel balls (using 4-ball wear test method, ASTM D 4172) showed 50% reduction when compared with similar test done with ZDDP.
5. Traces of MoS_2 based boundary film was observed on the wear scar of balls that performed well in lab test conditions.

Major Activities: Phase II Q1 (October 1, 2008 – December 30, 2008)

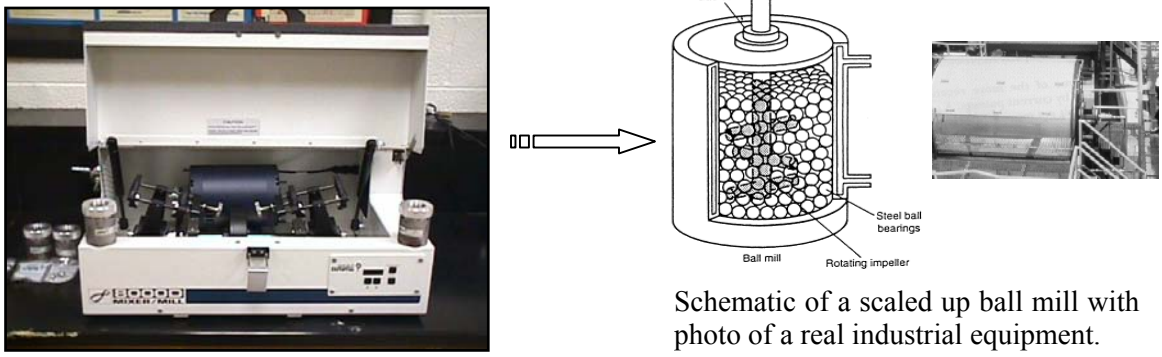
The project activities as outlined in the SOW for the funding phase Oct 1 through Dec 31, 2008 are noted below. Activities 1 and 2 are continuous in nature and will extend up to April 2009. The major activities of the team during this reporting period are:

1. Optimize selection and design of application-specific EP-EA additive (*Timeline: Oct'08 – Mar'09*)
2. Successful synthesis and characterization of application-specific EP-EA additive (*Timeline: Oct'08 – Apr'09*)

Task 1: Optimize selection and design of application-specific EP-EA additive

Results and Findings:

This phase primarily focused on the process optimization for making large batches of nanomaterials while maintaining the desired shape and size of the final product. Scale-up of this technology from lab-based set-up to semi commercial platform, was a key task for this program and for a successful drive to commercial viability of this technology. The challenge was to achieve the required size and shape without changing the chemistry and keeping the cost of production under control. The figure below presents the desired transition.



Schematic of a scaled up ball mill with photo of a real industrial equipment.

Left: Lab scale producing 50 gms in 96 hours; Right: large-scale ball mill capable of producing few kg every hour.

1. Particle size comparison using lab scale vs. commercial units

To understand the effect of parameters in large-scale milling of nanomaterials, two commonly used mills were explored (*Mill 1 and 2*). During this study, process parameters such as milling duration, milling media (*steel, hardness, ratio of ball to material*) and milling media (*dry vs. wet, presence of surfactants*) were considered for the optimization process. Samples were taken at regular intervals and analyzed for particle shape and size (*particle size distribution-by number*) and compared. Table below presents the nanomaterials particle size produced after milling in the lab unit and compared with the two large mills. The table shows the distribution of the particles within 10%, 50% and 90% range and also compares the quantity of production. Throughput in the large mills could be increased further if the requirement for nanomaterials increases.

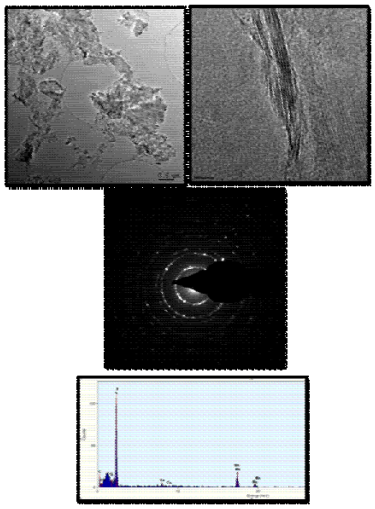
Table: Comparison of lab scale and large ball mill for production of Nanoparticles

Processing method	Duration of milling (hrs)	Quantity of production (gms)	Size (microns), number		
			10%	50%	90%
Raw material	0	NA	1.2	1.8	4.5
Lab scale mill	96	50	0.15	0.24	2.0
Large mill 1	3	2000	0.37	0.62	1.53
Large mill 1	6	2000	0.24	0.41	1.0
Large mill 2	3	1500	0.28	0.44	0.78
Large mill 2	6	1500	0.11	0.15	0.38

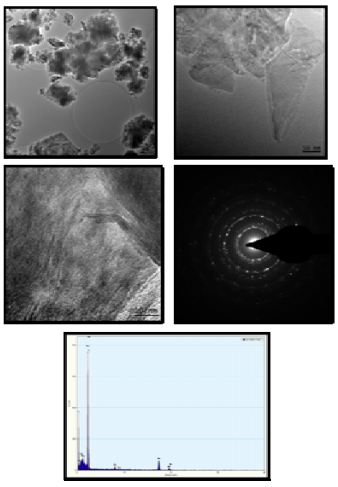
2. Particle shape comparison using lab scale vs. commercial units

The particle morphology of nanomaterials produced in large mills was investigated as it was important to understand the resulting shape of the nanoparticles and their variance from lab based processes. High-resolution transmission electron microscope (HRTEM) images and energy dispersive spectroscopy (EDS) indicated there

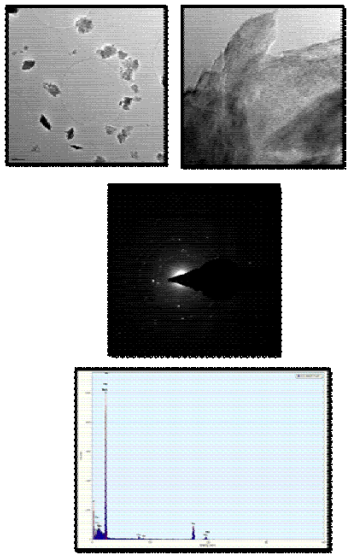
were no significant amorphisation or oxidation of the nanomaterials produced in bulk from commercial units. These results indicated that chemistry of the nanoparticles didn't change during processing (*this was a concern as the large mills could possibly initiate a chemical reaction between the materials or even significantly oxidize it*). To investigate this in detail, these processes were explored for 3 and 6 hours separately, and samples were analyzed. It was observed that after 6 hours it was possible to achieve the desired shape and size without any significant deterioration of the material.



TEM, electron diffraction pattern and EDS of milled nanoparticles after 6 hours of processing in large-scale mill (Company 1) in wet condition.



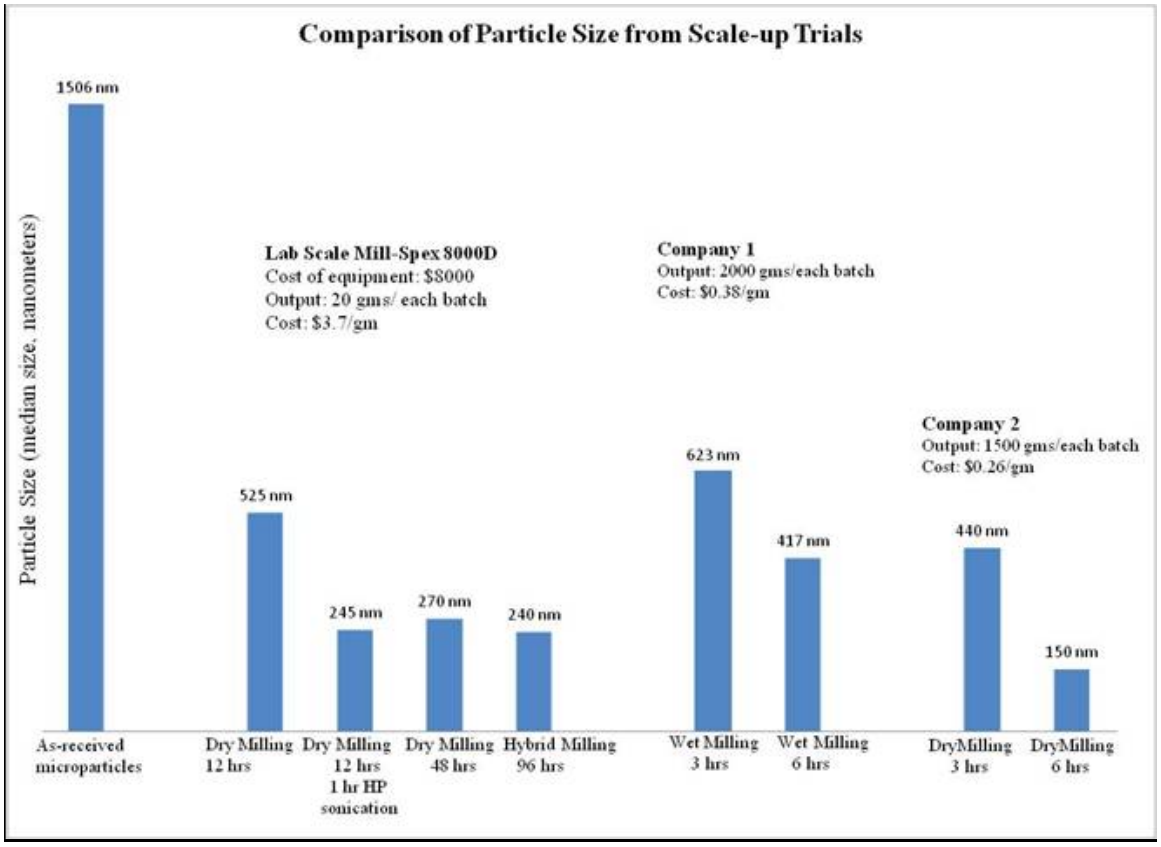
TEM, electron diffraction pattern and EDS of milled nanoparticles after 3 hours of processing in large-scale mill (Company 2) in dry condition



TEM, electron diffraction pattern and EDS of milled nanoparticles after 6 hours of processing in large-scale mill (Company 2) in dry condition.

3. Particle size comparison and estimated cost of production

Figure below presents the comparison of the final nanoparticle size and estimated cost of production for lab and commercial units. Plot shows that the scale-up approach could produce desired nanoparticles with adequate selection of process parameters. In addition, the cost also came down significantly as the volume of production was increased in the large mills. To understand the repeatability of this approach more tests should be performed and samples analyzed.



Comparison of final products of the lab-scale unit and two large-scale mills

Task 2: Successful synthesis and characterization of application-specific additive

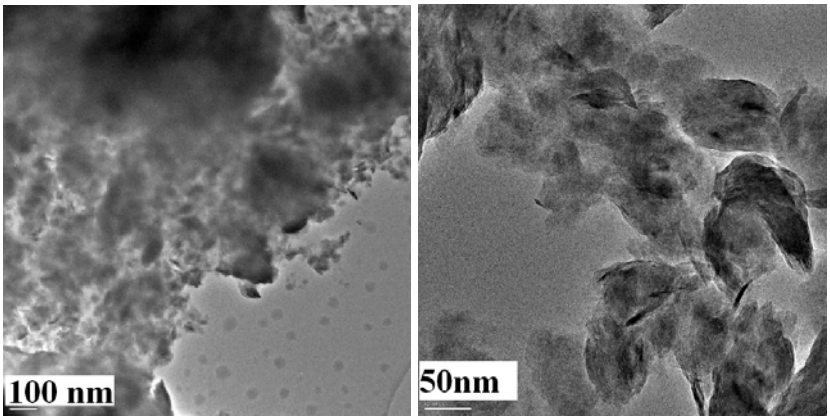
Results and Findings:

The team has identified and developed a multi-component nano-engineered inorganic and organic hybrid systems based on Ag, B and Mo chemistries to positively impact the low SAPS approach and also improve the friction and wear characteristics of the nanomaterials based additive in lab based tribological tests. Targeted multi-component design approach is presented in Fig. 1 (*pg. 7*) of this report.

The team developed a method to integrate these chemistries using a chemo-mechanical hybrid process to synthesize MoS_2 incorporated with nanoparticles of silver (*Ag, 5-10 nm in size*) as metallic dopant. The other designs include boron-based organic molecules or potassium triborate with MoS_2. Optimization of the parameters for hybrid milling process (*dry: wet phase ratio, milling time, and milling media*) is based on the results of prior experimental data (*reported in 2nd and 3rd Q DOE reports*) and was applied to the current designed formulations during the optimization process.

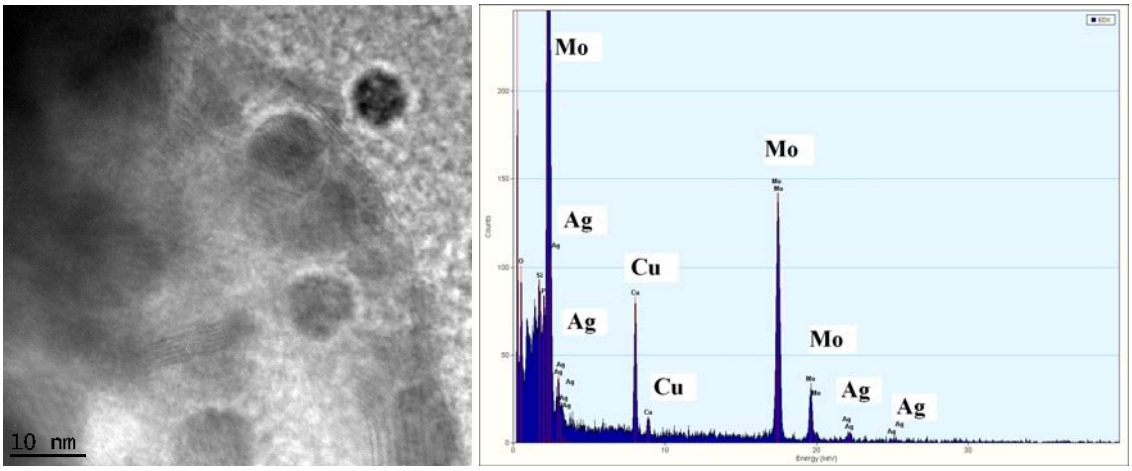
The samples were systematically analyzed using a series of analytical techniques (*TEM, EDX, and PSA analysis*), to confirm size, shape and chemical composition of the desired formulations. In *Formulation-1*(*hybrid milled MoS_2/potassium triborate nanoparticles*), the goal of preparation of nanoparticles with triborate core and MoS_2 shell was not fully achieved. Many potassium triborate particles didn't have molybdenum sulfide shells and were found loose in the dispersion (*figure below, left*). Besides, sample was highly agglomerated and difficult to disperse in oil.

In *Formulation 2*(*hybrid milled MoS_2/boron amide*) nanoparticles were uniformly ellipsoidal open-ended structures of MoS_2 nanoparticles with mean size 230 nm, and 90 % of particles smaller than 350 nm (*Figure below, right*). The particles were well dispersed and could be easy suspended in oil for a reasonable length of time (*6-7 days*) before beginning to show signs of settling down.

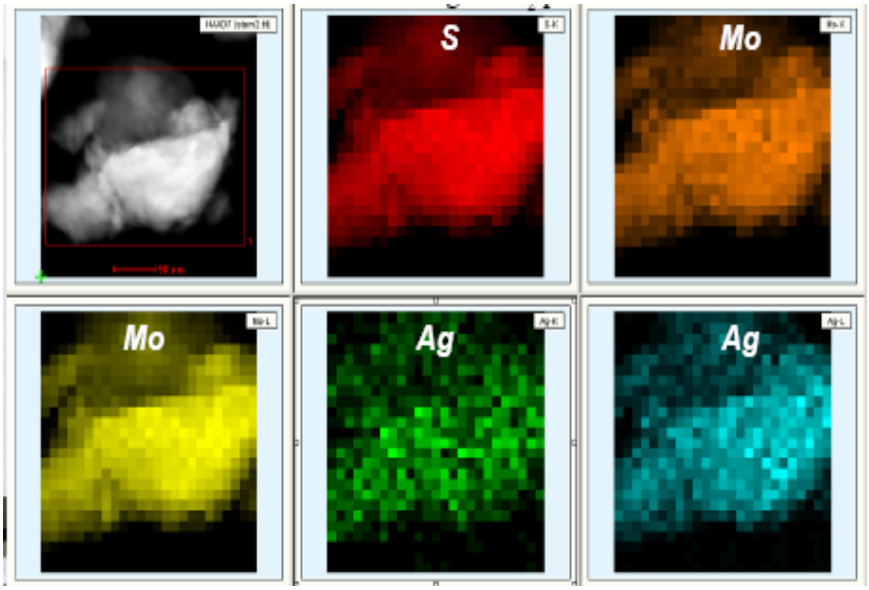


TEM graphs of hybrid milled MoS_2/potassium triborate (left) and MoS_2/boron amide (right) nanoparticles

In *Formulation 3* (*hybrid MoS_2 nanoparticles [average size of 200 nm] doped with Ag nanoparticles [average size of 10 nm]*) silver nanoparticles were incorporated into MoS_2 nanoparticles (*figure below*). Scanning-TEM/EDX mapping of MoS_2 nanoparticles showed uniform distribution of Ag-nanoparticles in the MoS_2 matrix.



TEM graph of hybrid milled MoS_2 incorporated with Ag nanoparticles and EDX pattern of MoS_2 nanoparticle



STEM/EDX mapping of hybrid milled MoS_2 nanoparticles incorporated with Ag nanoparticles (2% wt.)

Silver nanoparticles were incorporated in the MoS_2 nanoparticles in the form of silver thiomolybdate and/or molybdate phases. From literature review, such composite system was expected to dramatically improve the lubrication properties at higher temperatures (*300-700°C*).

Several strategies to incorporate silver nanoparticles in molybdenum sulfide were developed and tested:

1) Separate preparation of silver metal nanoparticles by reduction followed by combination with MoS_2 and hybrid milling,
2) Combined hybrid milling of silver salt and molybdenum sulfide followed by silver salt reduction.

Very diluted solution of silver salt was used for the preparation of silver nanoparticles. However, increasing concentration of reaction solution by solvent removal caused aggregation and led to large particles. The team is working to optimize the solvent removal process and use sodium citrate as a capping agent for Ag-nanoparticles and prevent their aggregation.

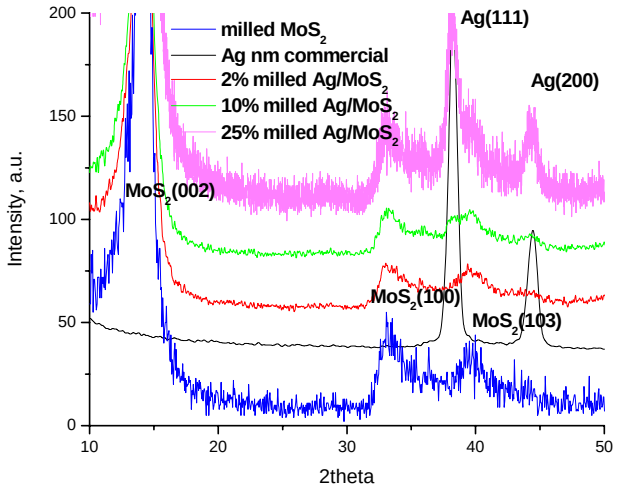
For the second strategy, which included a combined MoS_2 hybrid milling and Ag reduction, it was found that sodium tetrahydroborate reduced not only silver salt but also reacted with MoS_2. Milder reducing agent (*DMF*) was used to reduce $AgNO_3$ without interaction with MoS_2.

$$2\ Ag^{+} + HCONMe_2 + H_2O \rightarrow\ 2\ Ag^{0}\ + Me_2NCOOH + 2\ H^{+}$$

Further optimization of parameters for the synthetic process - time, conditions for Ag-nanoparticles extraction from solution and combined milling/reduction step are necessary.

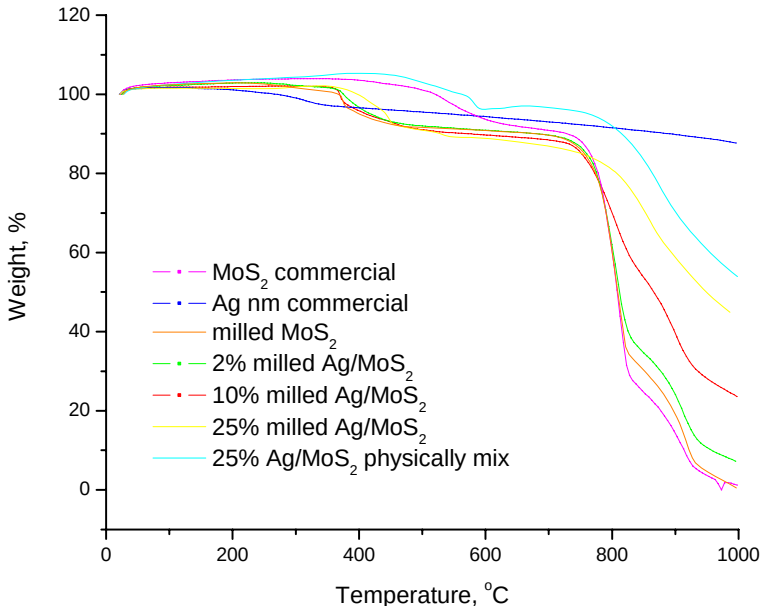
Low concentrations of small Ag-nanoparticles (≈*10 nm*) dispersed in MoS_2 nanoparticles (≈*200 nm*) made it difficult for their identification. Only a few analytical techniques are available to study nanoparticles in nanoparticles. Further addition of Ag-nanoparticles and increasing their concentration in MoS_2 can give more information on the interaction of silver with molybdenum sulfide.

Higher concentrations of Ag (*10 and 25 %wt.*) showed a good dispersion of Ag-nanoparticles in MoS_2 using powder XRD, while samples containing low %wt silver (*2% wt*) are essentially undetectable (*figure below*).

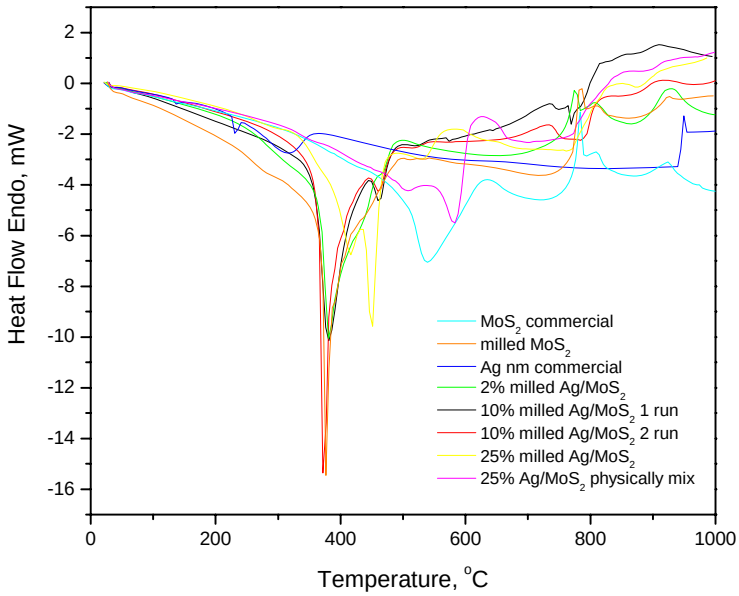


XRD analysis for Ag incorporated MoS_2 nanoparticles

Thermo gravimetric analysis (*TGA*) and differential scanning calorimetric (*DSC*) analyses were done to study the interaction of Ag with Mo at higher temperatures (*figures below*). Possible formation of silver molybdate was detected (*at 425ºC*) from the decomposition of MoS_2 nanoparticles and reaction with silver nanoparticles.



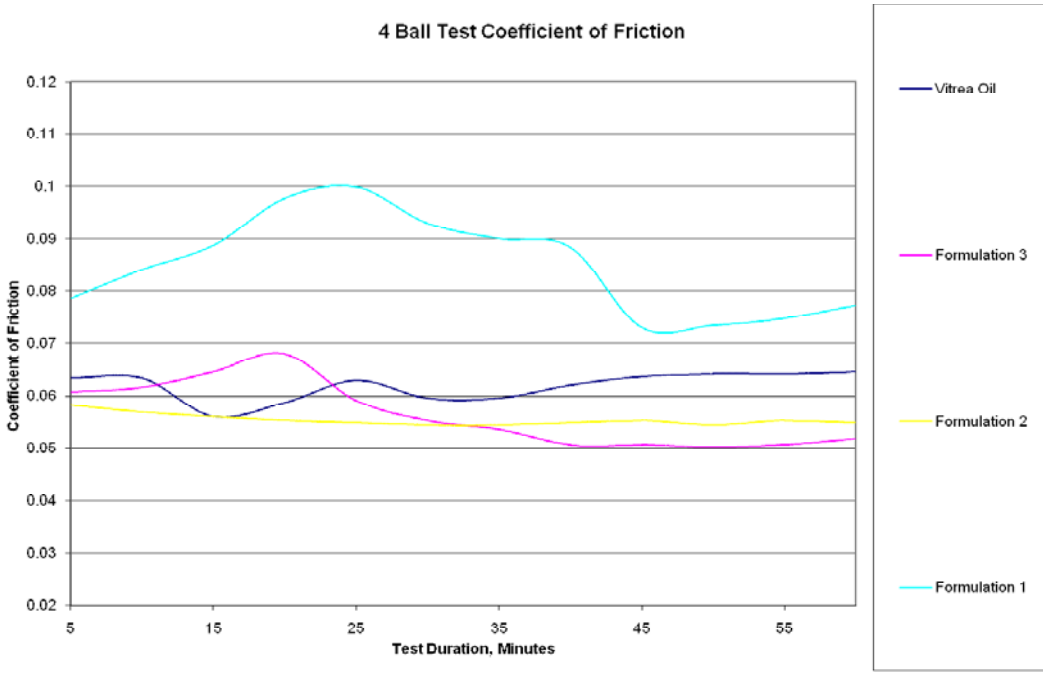
TGA analysis for Ag incorporated MoS_2 nanoparticles



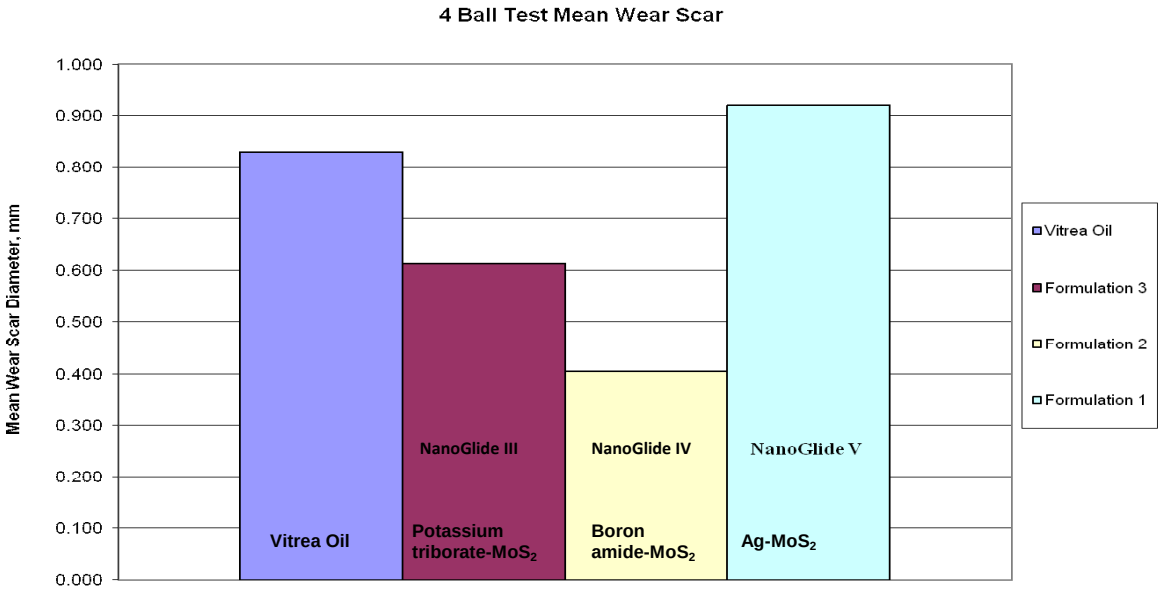
DSC analysis for Ag incorporated MoS_2 nanoparticles

1. Lab scale tribological evaluation of select nanomaterials in base oil

All samples were added in 1% by weight (*based on 1% wt of MoS_2 prepared samples*) to non-formulated base oil (*Vitrea 150 oil*). *Formulation 2* (hybrid milled MoS_2/boron amide) showed lowest mean values of coefficient of friction and wear scar diameter (*figures below*). *Formulations 1 (hybrid Ag-nanoparticle/MoS_2) showed no noticeable improvement in wear* scar size.



Lab-scale tribological evaluation of different formulations (4-Ball Test, Coefficient of friction)



Lab-scale tribological evaluation of formulations (Four Ball Test, Mean Wear Scar diameter)

Significant Conclusions and Accomplishments:

1. Efforts were made to scale up the process for nanoparticle development using commercial units with successful size and structure retention of the nanomaterials produced in kilogram quantities.
2. The proposed multicomponent nanoparticle formulations are:
   - molybdenum sulfide (good solid lubricant at moderate temperatures, <350°C),
   - silver nanoparticles (form silver molybdate which is a good lubricant at high temperature >400°C),
   - boron-based additive (potassium borate and boron amide are good extreme pressure additives).

3. The current material compositions were developed (Ag incorporated MoS_2, hybrid milled MoS_2/boron amide, and hybrid milled MoS_2/potassium triborate) for low SAPS applications and evaluated with lab tribo-tests.
4. Silver reduction process for synthesis of Ag nanoparticles was developed for adding Ag to MoS_2 during hybrid milling process. Optimization of process parameters for use of 'milder' reducing agent is still necessary.

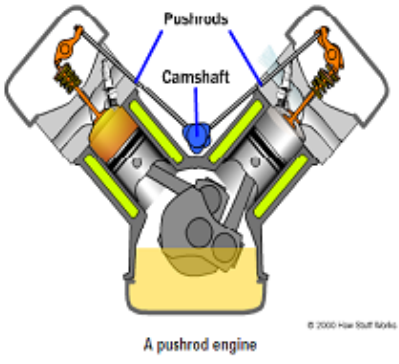
Major Activities: Phase II Q2 (January 1, 2009 – February 27, 2009

The project activity during the funding period Jan 1 through Feb 28, 2009 was:

1. *Component level test and single cylinder evaluation of nanoparticle based additive material for friction and wear reduction*

Engine test was designed to evaluate the effectiveness of nanoparticle-based additives to improve durability and efficiency. The team has investigated the effects of adding nanoengineered MoS_2 particles into engine oil (*15W40 formulated oil, provided by Caterpillar*). The engine test included two engines that would run for seven days, twenty-three hours per day. One engine will be filled with standard engine oil, while the other use the same oil with doped nanoparticles in certain predetermined percentage. Each engine (*Horizontal Shaft Overhead Valve 4 Stroke Gas Engine hooked to a generator [6.5 HP, 3600 RPM, 196 cc Engine Displacement, 2600 Watt]*) was hooked to a generator, which was wired to resistors to simulate varying load on the engine.

The objective was to design and develop an engineering test station to study the behavior and optimize the performance of nanoengineered MoS_2 lubricants to deliver low friction and wear properties. The success of this project will allow major value addition through, significant energy savings for power generation and vehicle engines (*in the long term*) as well as develop low SAPS lubricant additive technology for engine oils. This technology will potentially offer a substitute for ZDDP currently used.



A pushrod engine

1. Design of the test vehicle setup

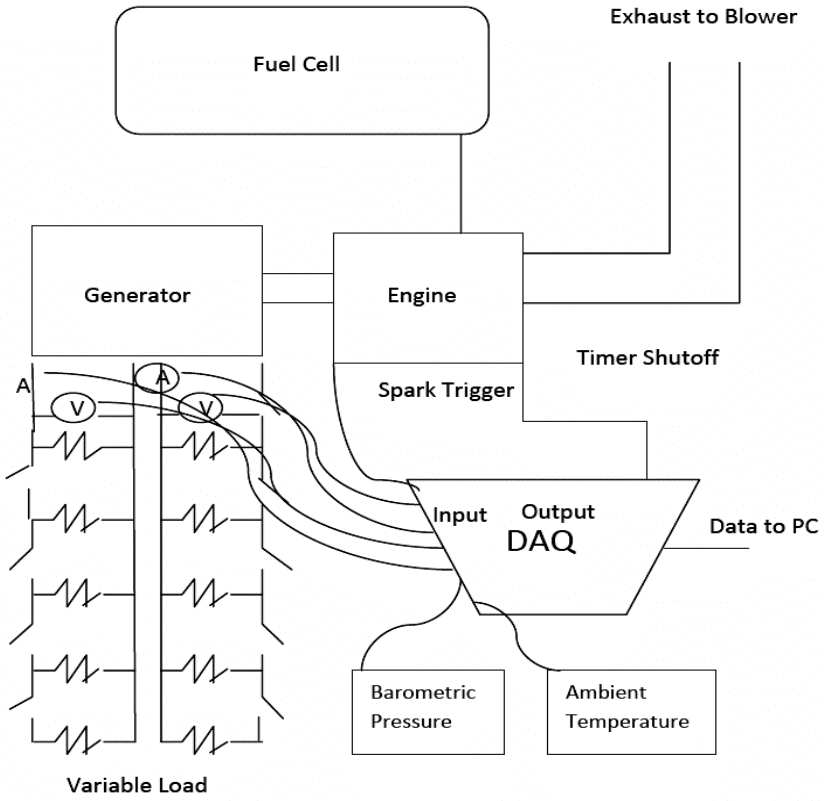
The engine test was developed to achieve three main goals: (1) to identify a suitable engine to perform the tests, (2) to design and develop an engine-based (figure below) test structure to validate nanoengineered lubricants for application specific testing, and (3) to demonstrate the validity of test structure for understanding tribological behavior of advanced lubricants under engine conditions.

The engine test was designed to evaluate the performance of nanoparticle additives to improve friction and wear characteristics. The team investigated the effects of adding *nanoengineered* MoS_2 particles into regular engine oil using the designed engine test set-up. The engine test used two engines that run for 7 days, 23 hours per day (*one hour service time*). One engine was filled with standard engine oil, while the other used the same oil plus predetermined amount of nanoparticles. Each engine was connected to a generator, which was wired to resistors to simulate varying load on the engine.

Voltage, current, and RPM readings were recorded during the engine run, which allowed power be plotted verses RPM, and provide information if there was a power gain due to friction reduction in the engine. Both engines to be disassembled before and after each run, and the mating surfaces analyzed for wear comparisons.

In the test structure, each engine was hooked to a generator, which was wired to resistors to simulate load on the engine (*figure below*). Switches were used to connect the resistors, such that the load could be varied. Software program 'LabView' was used to measure voltage, current, and RPM during the engine run, and allow power be plotted

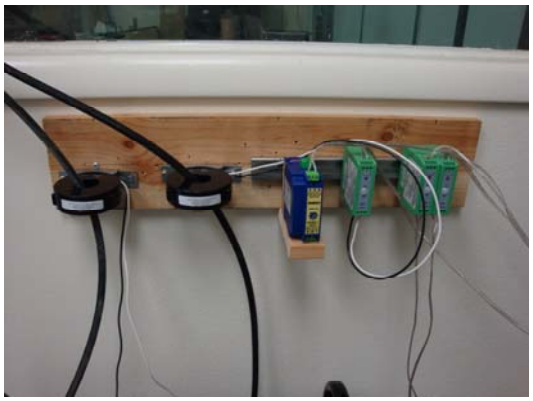
versus RPM. These readings will provide information if there was a power gain due to friction reduction in the engine.



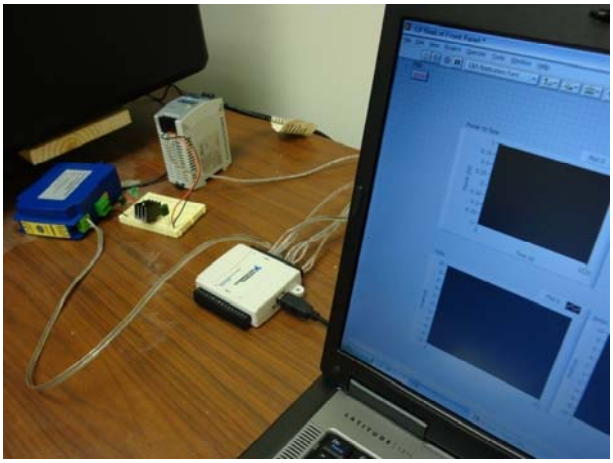
Design of the test set up

2. Engine test setup

Laboratory setup was designed (*figures below*) to test hybrid multi-component MoS_2 nanoparticles as an engine oil additive. Design parameters were indentified to test engine with and without MoS_2 based nanomaterials. Procedures were created for future experiment validation and all necessary safety requirements were evaluated and implemented.



General Engine Test Setup and Panel with Engine Sensors/Conditioners



Resistor Banks and Engine Control Center

Engine load was simulated with thirty-two 150-Ohm power resistors wired in parallel. Data from sensors were gathered using a National Instrument USB-6009 DAQ. Voltage and current transducers were used to obtain power output to resistors. RPM was obtained by using a Fluke RPM80 inductive pickup. Barometric pressure was measured using an Omega wall-mounted sensor. Temperature and humidity in the room were recorded using a standalone Omega USB device.

Each engine was disassembled for analysis before and after each test run. The replicas of surfaces of the camshaft, journals, bore, and rocker arm base were analyzed

with a profilometer to measure wear. Current and voltage measured by LabVIEW were multiplied to obtain power and was plotted against RPM obtained by the trigger on the spark plug wire. The room temperature, humidity, and pressure were also monitored. The difference in the oil temperature was measured using a thermocouple placed inside the drain plug (figure below, left). It was expected that the oil temperature would decrease as friction reduced due to the addition of MoS_2 based additive. Fuel consumption was measured using a load cell mounted underneath the fuel container (figure below, right). The rate of fuel weight change was monitored and converted into gallons per hour.

Oil Temperature Thermocouple and Fuel Consumption Load Cell

3. Real time data monitoring

For the LabVIEW program, each input from different sensors has to be configured using the 'DAQ Assistant' (figure below). The input for the voltage transducer was input 1, or simply 'DAQ Assistant'. The DAQ assistant will take 100 samples per second, and takes the mean of those values. This will be multiplied by the current input to gain the power reading. The amperage, which was located on the same wire, was run through a ferrite core current transformer.

The same set up exists in two separate circuits. Once the power has been found for both circuits, it will be then added to get total power. A meter can be seen on the

block diagram that will change every second, along with waveform graphs for amperage and voltage. This will tell if one of the circuits failed during testing.

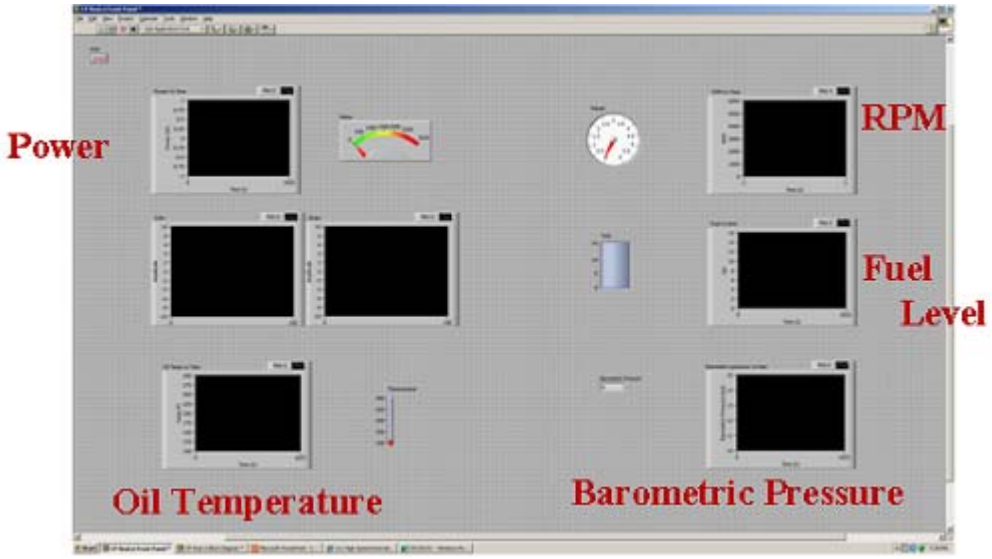
The RPM will be read from a trigger that will produce spikes each time there was a spark for combustion. These spikes will be turned into something that the DAQ can read, between zero and 10 volts. This will be 'DAQ Assistant5' and will count each time the spike reaches a predefined threshold voltage. The numbers of spikes in one-second multiplied by 120 will give RPM. [*it is multiplied by 120 because for every spark there are two rotations in the cylinder and 60 to get from seconds to minutes*]. This data will then be plotted versus time.

The next sensor is the thermocouple, LabVIEW 'DAQ Assistant6', and has been installed at the drain plug location to obtain temperature readings of the oil during testing. It uses a shielded cable since the output is in millivolts and this prevents electrical noise creeping into the final data output. This cable was then run to an amplifier, which converted the mV readings into a larger voltage [*so that the actual reading will be higher than the noise that corresponds with the given data*].

The load cell, LabVIEW 'DAQ Assistant7', was connected underneath the fuel tank. This load cell required an excitation voltage. When a weight was applied to the aluminum block, it registered the load depending on the deflection observed. [*The strain gauges connected to the aluminum block require an input voltage, and given that input voltage, the film will expand or contract and will change the voltage out reading that will be given by the conditioner. This conditioned output will be 12.6 volts in to the DAQ. The actual voltage will be changed by the resistance seen in the bridge, and will again be conditioned before being read by the DAQ. Again, it will be taking 100 data points per*

second, the mean value will be calculated and subtract by 17 (weight of dry tank, lb), which is simply a guess of how much the fuel cell weighs on the load cell. On the diagram, it can be seen that the value is then divided by 6.1 (lb/gal), which gives the pound force of gasoline per gallon. So every 6.1 pounds of force gives 1 gallon of fuel. These values will then be plotted versus time to find fuel consumption].

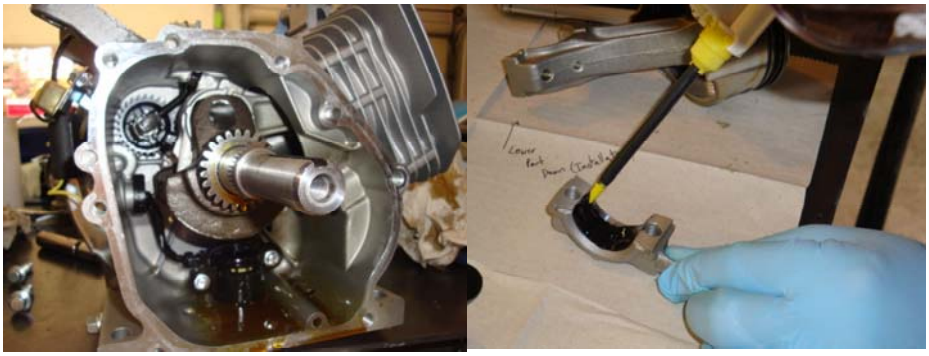
Finally, the barometric pressure sensor, 'DAQ Assistant8' outputs zero to 5 volts. Within the DAQ Assist was a table that allowed specifying a particular voltage reading with a corresponding pressure reading in pounds per square inch (psi).



LabVIEW Real Time Experiment Monitoring

4. Engine wear studies

Surface replication has been employed in engineering for many years, particularly for in-situ hi-resolution metallography. Microset replicating compounds have a resolution better than 0.1 microns (*4 x 10^{-6} inches*) and can be used not only for metallography but also for a multitude of other purposes including 3-D applications. These specially formulated two-part polymers are supplied in cartridges and are dispensed as fully mixed semi-viscous liquids, using simple dispensing guns and mixing nozzles. They cure quickly to produce flexible hi-resolution replicas, which can be peeled from the surface. When viewed under microscope under coaxial illumination, they have a bright metallic appearance, allowing details such as microstructure, micro cracking and pitting to be observed at high magnifications. These characteristics make the technique very suitable for the assessment of defects on critical engineering surfaces.

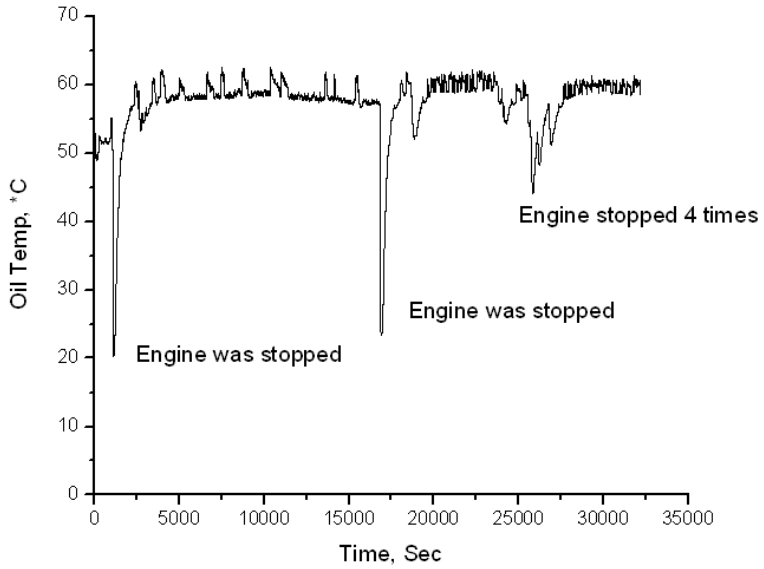


Open engine site and duplication of the surface parts using Microset kit

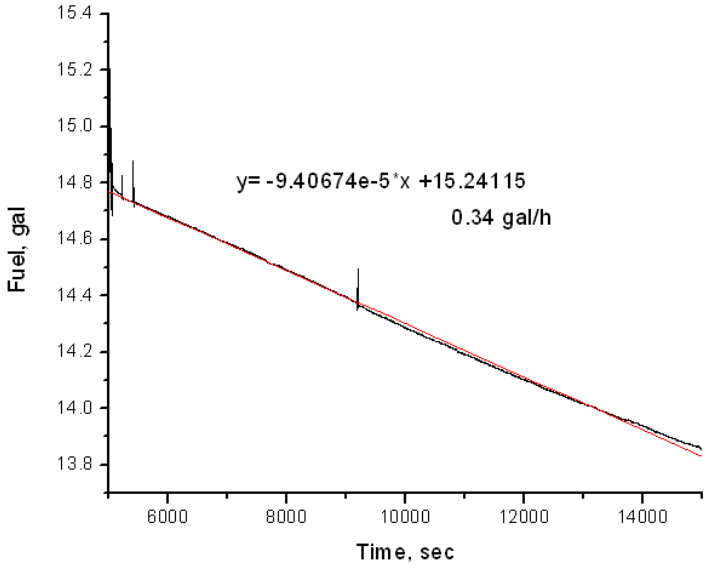
4. Engine tune-up studies

Engine tune-up was done to test the performance and response of sensors, align and calibrate their measurements. Various engine parameters (*power, rpm, oil temperature, fuel consumption*) and environment parameters (*barometric pressure, room temperature, humidity, and dew point*) were recorded while the engine was running with 15W40 oil. The loop time between engine parameter measurements was approximately

one second; the sum of loops gives the time length of the run. The engine oil temperature increased and held at 70°C during engine runs, and fell when engine was turned off (figure below). The following graph illustrates the fuel consumption rate for the engine tune-up test.



Engine Oil Temperature Measurements



Engine Fuel Consumption Rate

The linear fitting and correlation of the fuel consumption (figure above) showed very strong linear dependence R=0.9987 and gave a linear equation of y= -9.40674e-5*x +15.24115 and consumption rate of 9.4 e-5 gal/second or 0.34 gal/hour.

Conclusions and Recommendations

The design and development of a test vehicle for the nanoengineered lubricant has been very beneficial in understanding the working of a single cylinder engine and gaining knowledge of relevant components best suited for measuring wear. This also offers the opportunity to explore engineered nanomaterials and their application to real world problems. The tasks leading up to the engine test design helped understand the functioning of resistor, load cell, transducer, transformer and rpm sensor. This test design has also been helpful in gaining a better appreciation of workplace and environment safety.

Publications and presentations:

1. Technical presentation 'Multi-component Nanoparticle Based Lubricant Additive to Improve Efficiency And Durability in Engines' at the 14th Diesel Engine-Efficiency and Emissions Research (DEER) Conference August 4-7, 2008, Dearborn, MI

2. Synthesis, Challenges, and Functional Properties of Nanoparticles for Advanced Lubrication, Dmytro Demydov, Arpana Verma, Atanu Adhvaryu, Philip McCluskey, and Ajay Malshe, Annual STLE Meeting, Cleveland, OH may 19-22, 2008

3. CP-I project presentation and poster (2nd place award), Design and Development of a Test Vehicle for Nanoengineered Lubricant Additive for Sustainable Systems, Jason Bailey, Travis Florquist, Ajay Malshe, and Dmytro Demydov Mechanical Engineering Department, University of Arkansas, April 25th, 2008.

4. Multi-component Nanoparticle Lubricant Additives to Improve Efficiency and Durability in Engines, Technical Session Name: Fuels and High Performance Lubricants. The 14th Diesel Engine-Efficiency and Emissions Research (DEER) Conference, August 4-7, 2008, at the Hyatt Regency Dearborn in Dearborn, Michigan.

NOTE: Detailed procedure of the chemomechanical process and selection of the active chemical compounds are subjected to a US patent application (*from a separate research project and do not fall under the current DOE funded program*) and is therefore considered proprietary data not suitable for public release. The information is core of the current project activity and is also based on our past experience in technology development in a related area of application. It is therefore advised to the reader to please contact the Principal Investigators or the Project Director for further information. Principal Investigators (Co-PIs) listed below may be contacted for further details regarding the project and portions covered by intellectual property:

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Critical Project Path Milestones: